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Primary Processes in the Flash Photolysis of Dimethyl Carbonate Vapor

AUTHOR(S):

Ibuki, Toshio; Takezaki, Yoshimasa

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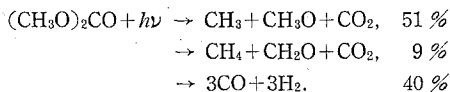
Toshio IBUKI and Yoshimasa TAKEZAKI*

(Takezaki Laboratory)

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The photochemical primary processes of gas-phase dimethyl carbonate have been studied by means of flash method.

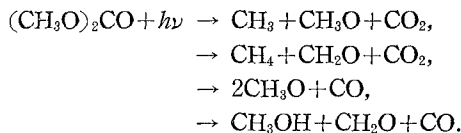
On the basis of the observed products, *i. e.* carbon monoxide, carbon dioxide, methane, ethane, dimethyl ether, methanol, formaldehyde and hydrogen, the following primary processes and the relative extents of contribution have been proposed :



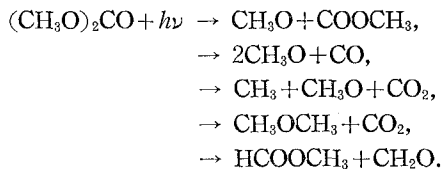
INTRODUCTION

Recently, dialkyl carbonates have received attentions as a source of alkoxy radicals, and some papers have been published as to the mode of decomposition ; however, the opinions for this are rather divergent. Wijnen¹⁾ and Thynne and Gray²⁾ have reported that dimethyl carbonate (DMC) decomposes thermally at the temperatures about 120°C, yielding dimethyl ether and carbon dioxide in equivalent amounts by heterogeneous reaction. On the other hand, Gordon and Norrish³⁾ found no evidence for thermal decomposition of the carbonate in a quartz cell even at 350°C.

Using full radiation of a medium pressure mercury arc, Wijnen⁴⁾ has proposed the following primary steps on the basis of the fact that the major product was methanol ;



Yee Quee and Thynne⁵⁾ also studied the decomposition processes of dimethyl carbonate by the full light of medium pressure mercury arc and reported that the primary steps are



* 伊吹 紀男, 竹崎 嘉真

Meanwhile, Gordon and Norrish³⁾ reported that the photolysis at 350°C with the similar mercury arc yielded only traces of methane, carbon monoxide and carbon dioxide.

With the aim of screening the most plausible primary processes among those various possibilities, dimethyl carbonate has been photolyzed using a flash lamp; however, the derived mechanism therefrom seems to differ in detail from any of the results so far reported.

In this investigation, flash photolysis has been used with the intention to reduce the radical-molecule secondary reactions; the high concentrations of radicals generated by flash should strongly favor the recombination or disproportionation of them, and the reaction products would reflect the results of those inter-radical reactions. However, this intention does not seem to have been met with satisfactorily.

EXPERIMENTALS

Apparatus and Procedure

The flash lamp, made of quartz tube of 10 mm diam. with 1 mm wall thickness, was sealed coaxially with O ring in the center of a cylindrical glass reaction cell (350 cc, *ca.* 50 mm ϕ × 200 mm). The photolysis was carried out by discharging the energy of 500 J per flash (40 μ F, 5000 V) through the lamp, which was filled with a few drops of mercury and argon at 80 mmHg. The flash duration was about 100 μ sec at half peak-intensity. All experiments were made at room temperature.

The reaction products were drawn out by Töpler pump through a trap cooled with dry ice-methanol mixture or with liquid nitrogen, then the products were analyzed mainly by gas chromatography. Formaldehyde was determined colorimetrically by fuchsin coloration.

In the photolysis of dimethyl carbonate in the presence of ethylene-d₄, three hydrogen isotopes, H₂, HD and D₂, were analyzed quantitatively by means of TOF mass spectrometer, where the average value of the sensitivities of H₂ and D₂ was adopted as the sensitivity of HD.

Materials

Dimethyl Carbonate; Guaranteed reagent, the volatile materials (mainly methanol) were pumped off while solidified at about -70°C. Gas chromatogram showed no impurity.

Nitric Oxide; Prepared by dropping H₂SO₄ into the aq. solution of KNO₂ and KI⁶⁾. After washing and drying, purity was 98.8% as determined by gas chromatography (molecular sieves 5A, 2m, 26°C), the remainder being solely nitrogen.

Ethylene-d₄; 99 atomic %, supplied by Merch Scharp & Dohme of Canada Ltd.

Ethylene; Purity 99.9%.

RESULTS AND DISCUSSION

The absorption coefficient of gaseous dimethyl carbonate is not available, but Gordon and Norrish²¹ have reported that the carbonate absorbs the light shorter than 2000 Å.

In our experiments, when Vycor glass was used as a filter in order to cut off the light shorter than 2200 Å, no photolysis took place in spite of being irradiated by the lines of mercury longer than 2537 Å. Moreover, larger quantities of products were produced when the substance was irradiated by the lamp which contained mercury than with the lamp containing argon alone. These facts suggest that the light effective for the photolysis of dimethyl carbonate is the 1849 Å line of mercury since the argon used here must scarcely emit the light from 1700 to 2000 Å²¹.

After 30 flashes (total flash duration is about 3 msec; *ca.* 5% decomposition), the observed products were carbon monoxide, carbon dioxide, hydrogen, methane, ethane, dimethyl ether, methanol and formaldehyde, and no other higher hydrocarbons or higher compounds containing oxygen were detected.

Judging from the absorption coefficients²¹ of these products, those except for formaldehyde scarcely or do not have possibility to decompose by the succeeding flashes. Formaldehyde was found to decompose only about 1% when it was flashed at the concentration about equal to what was produced after 30 flashes of dimethyl carbonate, suggesting that under the present conditions formaldehyde will not undergo any appreciable secondary decomposition. Moreover, studies²¹ of reactions of dimethyl carbonate with radicals have shown that methyl or methoxy radicals reacting with dimethyl carbonate do not yield carbon monoxide. Therefore it must be natural to presume that carbon monoxide found in the present experiments is produced only in the primary processes. Thus all quantitative treatments will be expressed by the relative value with respect to carbon monoxide.

Table 1. Relative amount of the flash photolysis products of dimethyl carbonate in the presence of nitric oxide.

Capacity=40 μ F. Voltage=5000 V. No. of flashes=30

Initial conditions	DMC (mmHg)	21.0	20.0	20.2
	NO (mmHg)	0	19.9	23.8
	(NO)/(DMC)	0	0.995	1.18
Products	CO	1.00	1.00	1.00
	CO ₂	1.49	1.49	
	CH ₄	0.780 (CH ₄) _{obs}	0.254 (CH ₄) ₍₂₎	
	C ₂ H ₆	0.385	0.02	
	CH ₃ OCH ₃	0.122		0
	CH ₃ OH	0.552		0
	H ₂	0.977		0.944
	CH ₂ O	0.94	≤0.94	
	Material balance	C _{3.0} H _{6.0} O _{2.9}		

Flash Photolysis of Dimethyl Carbonate

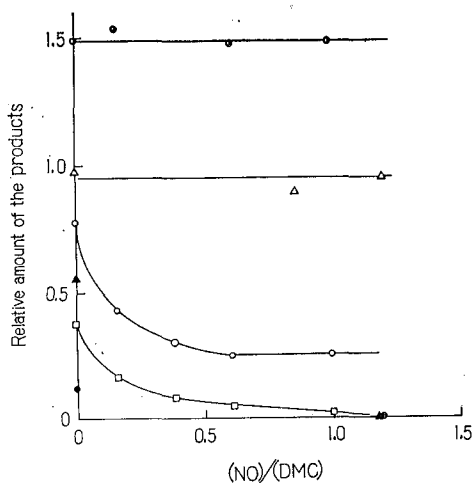
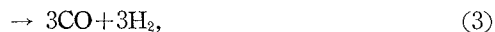
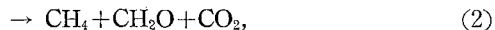
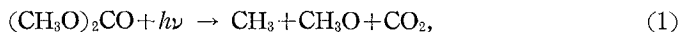


Fig. 1. Variation of the yields of products relative to carbon monoxide with (NO)/(DMC) ratio : \bullet , CO_2/CO ; \triangle , H_2/CO ; \circ , CH_4/CO ; \square , $\text{C}_2\text{H}_6/\text{CO}$; \blacktriangle , $\text{CH}_3\text{OH}/\text{CO}$; \bullet , $\text{CH}_3\text{OCH}_3/\text{CO}$.

Table 1 and Fig. 1 show the results of the flash photolysis of dimethyl carbonate in the presence of nitric oxide. From the figure we see that when the ratio of nitric oxide to dimethyl carbonate, (NO)/(DMC), exceeds unity only carbon monoxide, carbon dioxide, hydrogen, methane and formaldehyde are produced, and that ethane, dimethyl ether and methanol, which are found in the absence of nitric oxide, do not appear.

This suggests that carbon monoxide, carbon dioxide, and some parts of formaldehyde and methane are produced through molecular detachment processes in the primary decomposition, and that ethane, dimethyl ether and methanol are formed by radical reactions. Also, since the latter compounds can be formed by the reactions of methyl and methoxy radicals, the production of these radicals must have occurred in the primary steps.

Now the following processes may be assumed as the probable steps which are able to explain the experimental facts, the appropriateness of which will be examined below :



where reaction (3) is assumed from a stoichiometric relation that even in the presence of nitric oxide the ratio of hydrogen to carbon monoxide is almost unity. In the following discussion the hydrogen will be treated as being produced by molecular mechanism for the moment, and discussion will be given later in detail whether the atomic hydrogen is participating or not.

If both carbon monoxide and carbon dioxide are produced in the primary steps (1)~(3), the ratio $(\text{CO}_2)/(\text{CO})$ should be constant independently of the co-existence of radical reactions. Actually, this ratio is 1.49 independent of the added nitric oxide (See Table 1 and Fig. 1). Then, using this value the propor-

tions of reactions (1) and (2) are calculated by the following manner.

From reactions (1)~(3), we have

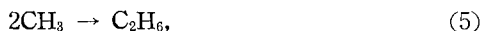
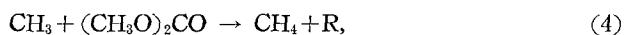
$$\frac{\text{Reaction (1)} + \text{Reaction (2)}}{\text{Reaction (1)} + \text{Reaction (2)} + \text{Reaction (3)}} = \frac{(\text{CO}_2)}{(\text{CO}_2) + (\text{CO})} = 0.60,$$

and

$$\frac{\text{Reaction (3)}}{\text{Reaction (1)} + \text{Reaction (2)} + \text{Reaction (3)}} = 0.40,$$

where parentheses represent the concentration of each substance.

If methyl radical is produced by reaction (1), the production and distribution of methane, ethane and dimethyl ether may be explained by the following reaction mechanism ;



On the other hand, methyl radicals might react with methoxy radicals, yielding methane and formaldehyde, *i. e.*,



If reaction (6') occurs, total amount of methane should decrease according as the disappearance of methyl and methoxy radicals when nitric oxide is added. However, as may be seen in Fig. 1, the amount of methane attains a steady value when (NO)/(DMC) becomes larger than 0.6, while ethane tends to decrease to zero at the point (NO)/(DMC) \approx 1.2, suggesting that despite of the presence of methyl radicals in the range of (NO)/(DMC) between 0.6 and 1.2, this radical does not form methane ; therefore reaction (6') must be negligible.

The above mechanism, reactions (1)~(6), makes the evaluation of the relative rate of reaction (1) to reaction (2) possible, *viz.*,

$$\frac{\text{Reaction (1)}}{\text{Reaction (2)}} = \frac{(\text{CH}_4)_{(4)} + (\text{DME}) + 2(\text{C}_2\text{H}_6)}{(\text{CH}_4)_{(2)}} = 5.58, \quad (\text{A})$$

where $(\text{CH}_4)_{(4)} = (\text{CH}_4)_{\text{obs}} - (\text{CH}_4)_{(2)}$, and $(\text{CH}_4)_{(2)}$ and $(\text{CH}_4)_{(4)}$ are the methane concentration formed by reaction (2) and reaction (4), respectively, and $(\text{CH}_4)_{\text{obs}}$ refers to what is found when nitric oxide is absent, and (DME) is the concentration of dimethyl ether (See Table 1).

Then we get

$$\begin{aligned} & \frac{\text{Reaction (1)}}{\text{Reaction (1)} + \text{Reaction (2)} + \text{Reaction (3)}} \\ &= \frac{\text{Reaction (1)}}{\text{Reaction (1)} + \text{Reaction (2)}} \times 0.60 = 0.51 \end{aligned}$$

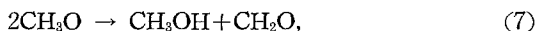
and

$$\frac{\text{Reaction (2)}}{\text{Reaction (1)} + \text{Reaction (2)} + \text{Reaction (3)}} = 0.09.$$

The total amount of methoxy radicals which must have been produced by reaction (1) can be estimated from the value of Eq. (A), namely,

$$(\text{CH}_3\text{O}) = \frac{\text{Reaction (1)}}{\text{Reaction (1)} + \text{Reaction (2)}} (\text{CO}_2) = 1.26(\text{CO}). \quad (\text{B})$$

So far we have discussed mainly about the processes with which methyl radicals disappear. As to the reactions of methoxy radical, there has been found methanol in the observed products as the methoxy containing compounds other than dimethyl ether formed by reaction (6). The following processes of methanol formation may be conceivable ;



If reaction (7) is predominant, the total amount of methoxy radicals is calculated as

$$(\text{CH}_3\text{O}) = (\text{DME}) + 2(\text{CH}_3\text{OH}) = 1.22(\text{CO}). \quad (\text{C})$$

Since the values of Eq. (B) and Eq. (C) are in good agreement, reaction (7) may be presumed to be one of methanol forming processes. On the other hand, the amount of methoxy radicals estimated from the balance of methoxy group with the assumption that the reaction (7') is important disagrees exceedingly with that of Eq. (B) calculated from the quantities of the products from the methyl radical reactions. Accordingly reaction (7) must make a principal contribution to the methanol formation.

Now, according to the proposed scheme, formaldehyde is formed by reaction (2) and reaction (7), then the amount of which can be calculated to be

$$(\text{CH}_2\text{O})_{\text{calc.}} = (\text{CH}_4)_{(2)} + (\text{CH}_3\text{OH}) = 0.81(\text{CO}),$$

while the observed value is 0.94 (CO) in fair agreement with the calculated. Thus the assumption of reactions (2) and (7) as formaldehyde-forming steps does not conflict with the observed facts.

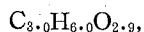
The mechanism involving reactions (1)~(7) requires the following relationships ;

$$\frac{(\text{CH}_4)_{\text{obs}} + 2(\text{C}_2\text{H}_6) + (\text{DME})}{(\text{CO}_2)} = 1.0 \quad (\text{D})$$

and
$$\frac{(\text{CH}_4)_{(2)} + 2(\text{CH}_3\text{OH}) + (\text{DME})}{(\text{CO}_2)} = 1.0. \quad (\text{E})$$

The calculated values of Eq. (D) and (E) from the observed products are 1.1 and 0.99, respectively, indicating the good agreement with the theoretical.

Finally, material balance of the observed products leads to



which is the same as the molecular formula of dimethyl carbonate, suggesting that any significant fraction of the decomposed carbonate has not been used to form other products.

In the above treatment molecular hydrogen formation by reaction (3) has been assumed. Now, the investigations, made in order to decide whether the hydrogen is generated by molecular detachment process or by atomic process, will be described.

Robb *et al.*⁹⁻¹³⁾ have reported that olefins are good scavengers of hydrogen atoms, $\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5$, and the utilization of ethylene- d_4 will make it possible to distinguish between hydrogen produced from dimethyl carbonate and those from ethylene, since ethylene also produces H_2 and H atom photochemically in the following manner^{13-17,20)};



and, when the mixture of ethylene- d_4 and dimethyl carbonate is photolyzed, the presence of hydrogen and deuterium will prove the production of molecular hydrogen, and on the other hand, if atomic hydrogen is produced, only deuterium will be found.

Table 2. Isotopic results for the flash photolysis of mixtures of ethylene- d_4 and dimethyl carbonate.

Capacity=40 μF . Voltage=5000 V. No. of flashes=50

Initial conditions	DMC (mmHg)	25.2	21.1	21.2	22.0
	C_2D_4 (mmHg)	10.8	10.5	18.2	41.0
	(DMC)/(C_2D_4)	2.33	2.01	1.17	0.537
% of total hydrogen produced	H_2	27.4	24.4	17.1	9.88
	HD	24.5	25.2	21.3	14.12
	D_2	48.1	50.4	61.6	76.0

Table 2 shows the distribution of hydrogen isotopes found in the flash photolysis of the mixture of dimethyl carbonate and ethylene- d_4 ; clearly there exists hydrogen deuteride.

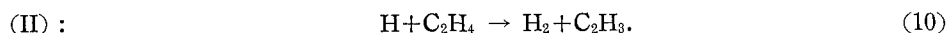
Possible processes leading to hydrogen deuteride are,

- (I) The secondary decomposition of the products produced by the reactions of ethyl radicals formed by addition of atom to ethylene- d_4 .
- (II) D atom abstraction by H atom from ethylene- d_4 .
- (III) D or H atom abstraction by H or D atom from D_2 or H_2 , respectively.
- (IV) Recombination reaction of H and D atoms.
- (V) H atom abstraction by D atom from dimethyl carbonate.

The possibilities (I)~(IV) are eliminated by the following reasons.

(I): Studies^{16,17)} of the reaction of hydrogen atom with ethylene have shown that the products found are *n*-butane, ethane and ethylene produced by ethyl radical recombination or disproportionation reaction. *n*-Butane and ethane are not decomposed by the light of 1849Å, since these compounds do not absorb this light⁹⁾.

In the present experiments, the total amount of butene-1, butene-2 and the other higher hydrocarbons except *n*-butane was below 4% of hydrogen, indicating possibility (I) to be unimportant.



It is known that reaction (10) occurs only at high temperature^{18,19)}. If reaction (10) took place in the present flash photolysis butadiene should be

definitely formed along with acetylene and this recombination product must be almost one half the disproportionation reaction products, C_2H_2 and C_2H_4 , as judged from the report of Tickner and Le Roy²¹⁾.

In order to ascertain this, ethylene has been photolyzed under the condition that the initial pressure is 21.5 ± 0.5 mmHg and the number of flashes is from 5 to 30. The gas chromatographic analysis has revealed that the amounts of products, relative to $H_2 \equiv 1.00$, are $C_2H_2 = 1.39$, n -butane = 0.05, and butadiene = $0 \sim 0.0003$. Therefore the possibility of (II) can be omitted.



The rate constant of reaction (11) varies from the order 10^5 1/mole·sec at $300^\circ K$ to 10^9 1/mole·sec at $1000^\circ K$ ²²⁾.

In the present studies, the reaction temperature during the photolysis has not been measured, so it is not obvious to what degree the temperature has been raised by flashes. However, even if the temperature rose instantaneously up to a few hundreds²³⁾, the rate constant would be of the order 10^7 1/mole·sec.

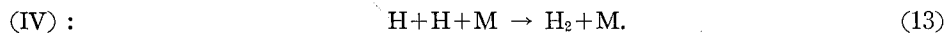
On the other side, the rate constant of the following reaction is of the order of 10^8 1/mole·sec⁹⁾ ;



Then the relative rate of reaction (11) to (12), R_{11}/R_{12} , must be

$$\frac{R_{11}}{R_{12}} \leq 10^{-1} \frac{(\text{Hydrogen})}{(\text{Ethylene})},$$

where (Hydrogen)/(Ethylene) is below 0.1 under the present conditions. Thus, we have $R_{11}/R_{12} < 10^{-2}$, which excludes the occurrence of (III).



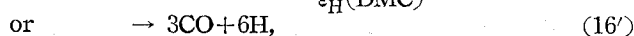
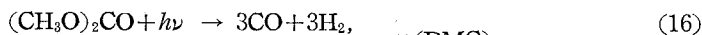
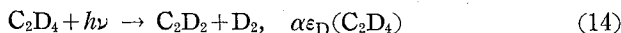
The rate constant of this reaction for $M = \text{DMC}$ is not available, but it must be about 10^{10} 1²/mole²·sec, as estimated from the value $k_{13} < 3 \times 10^{10}$ obtained for water²⁴⁾ as the third body.

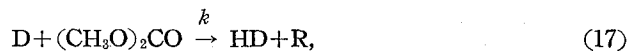
Then, R_{13}/R_{12} is

$$\frac{R_{13}}{R_{12}} = \frac{10^{10}(H)(M)}{10^8(C_2D_4)}.$$

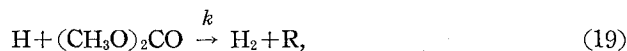
Since $(M)/(C_2D_4)$ is below 3 and (H) is estimated to be smaller than 10^{-4} atom/1/flash, both under the conditions of Table 2, we have $R_{13}/R_{12} < 10^{-2}$, and (IV) must be unimportant.

(V) : As in other hydrogen abstraction reactions by hydrogen atom we have to assume that hydrogen deuteride can be formed by this reaction, then the following reaction scheme seems to be plausible :





When reaction (16') occurs,



where α represents the fraction of the light which leads to reaction (14) in the total light absorbed by ethylene, and β that referring to reaction (15), and ϵ_D and ϵ_H are the absorption coefficients of ethylene- d_4 and dimethyl carbonate, respectively.

Isotopic effects will be neglected in the following kinetic treatments.

The above scheme yields the following rate equation independently of whether the molecular or atomic hydrogen is produced ;

$$\frac{R_{D_2}}{R_{HD}} = \frac{\alpha}{2\beta} \left(1 + \frac{k'}{k} \cdot \frac{1}{X} \right), \quad (F)$$

where X represents the ratio $(\text{DMC})/(\text{C}_2\text{D}_4)$.

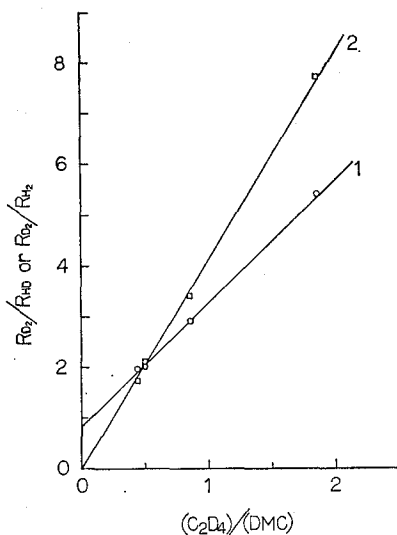


Fig. 2. Plots of R_{D_2}/R_{HD} and R_{D_2}/R_{H_2} against $(\text{C}_2\text{D}_4)/(\text{DMC})$ ratio.

Curve 1 : plot of R_{D_2}/R_{HD} against $(\text{C}_2\text{D}_4)/(\text{DMC})$,

Curve 2 : plot of R_{D_2}/R_{H_2} against $(\text{C}_2\text{D}_4)/(\text{DMC})$.

The experimental data are plotted in Fig. 2, curve 1, satisfying Eq. (F), and we get

$$\frac{\alpha}{\beta} = 1.68 \quad \text{and} \quad \frac{k'}{k} = 2.89.$$

The value of α/β shows that reaction (14) occurs to the extent of 63% and

reaction (15) to 37 % at 1849Å, being in fair agreement with the results of Tanaka and Akimoto¹⁵⁾, *i. e.*, reaction (15) 39 % at 1634Å + 1657Å and 28 % at 1930Å.

Now, discussions will be divided into two cases according to whether molecular hydrogen (reaction (16)) or atomic hydrogen (reaction (16')) is formed.

(a) In the case of the molecular hydrogen formation.

In this case, reactions (16'), (19) and (20) are omitted and the following relations can be derived ;

$$\frac{R_{D_2}}{R_{H_2}} = \frac{\alpha \varepsilon_D}{3 \varepsilon_H} \left(\frac{1}{X} \right), \quad (G)$$

$$\text{and} \quad \frac{R_{H_2}}{R_{HD}} = \frac{3 \varepsilon_H}{2 \beta \varepsilon_D} \left(X + \frac{k'}{k} \right). \quad (H)$$

(b) In the case of atomic hydrogen formation.

The reaction scheme except reaction (16) yields ;

$$\frac{R_{D_2}}{R_{H_2}} = \frac{\alpha \varepsilon_D}{6 \varepsilon_H} \cdot \frac{1}{X} \left(1 + \frac{k'}{k} \cdot \frac{1}{X} \right), \quad (I)$$

$$\text{and} \quad \frac{R_{H_2}}{R_{HD}} = \frac{3 \varepsilon_H}{\beta \varepsilon_D} X. \quad (J)$$

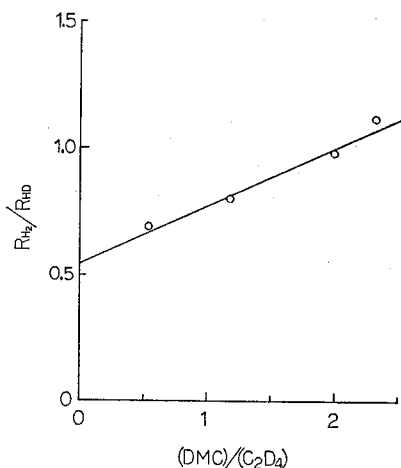


Fig. 3. Plot of R_{H_2}/R_{HD} against $(DMC)/(C_2D_4)$.

The plots of the observed R_{D_2}/R_{H_2} against $1/X$ and the observed R_{H_2}/R_{HD} against X are shown in Fig. 2, curve 2 and Fig. 3, respectively. As may be seen from these figures, the data of Table 2 satisfy Eq. (G) and (H), but do not Eq. (J) since the curve in Fig. 3 does not pass through the origin at all. Further, Eq. (I) is rewritten into

$$(R_{D_2}/R_{H_2})(X) / \left(1 + \frac{k'}{k} \cdot \frac{1}{X} \right) = \frac{\alpha \varepsilon_D}{6 \varepsilon_H} = \text{constant}, \quad (I')$$

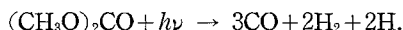
and the left-hand side of Eq. (I'), which can be calculated with the value of k'/k

Table 3. Calculations of the left-hand side of Eq. (I')

$X = (\text{DMC})/(\text{C}_2\text{D}_4)$	$(R_{\text{D}_2}/R_{\text{H}_2}) (X)/(1 + (k'/k)(1/X))$
2.33	1.81
2.01	1.71
1.17	1.15
0.537	0.648

obtained from Eq. (F), should be constant, contrary to the observation given in the second column of Table 3. Therefore the assumption of atomic hydrogen formation must be ruled out.

Moreover, thermodynamic calculations reveal that the energies are deficient by about 220 kcal., if all of hydrogen are generated *via* atomic hydrogen with the light of 1849Å. However, there may occur a reaction in which the hydrogen is produced partly as molecules and partly through atoms, *e. g.*,



Present studies have nothing to tell about the occurrence of such reactions.

Among the possible processes of the production of hydrogen deuteride, the possibilities (I)~(IV) have been ruled out, but in the separate photolysis of a mixture of ethylene and ethylene- d_4 (initial pressure was 29.4 mmHg at 22.0°C, $(\text{C}_2\text{D}_4)/(\text{C}_2\text{H}_4) = 1.51$, 5 flashes), the isotopic composition of hydrogens has been found as $\text{H}_2 = 30.0\%$, $\text{HD} = 29.4\%$ and $\text{D}_2 = 40.6\%$. This fact may indicate that (IV) can not be ruled out when high concentration of hydrogen atoms is produced by a flash. However, since the inclusion of the recombination reaction of atoms makes the rate equations so complicated and insoluble analytically, discussion has been given only for the reaction scheme without this reaction; therefore, though the conclusion given here that the primary processes will form molecular hydrogen must be very plausible, we can not exclude entirely the occurrence of the reaction which produces hydrogen atom partly.

CONCLUSION

From the observed reaction products in the flash photolysis of dimethyl carbonate vapor, reactions (1), (2) and (3) have been deduced as the primary steps, and radical reactions (4), (5), (6) and (7) as the secondary reactions, with which the nature and distribution of the products can be explained reasonably. And from the relative value of the products, the relative extents of the primary processes have been estimated as reaction (1) 51%, reaction (2) 9% and reaction (3) 40%.

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